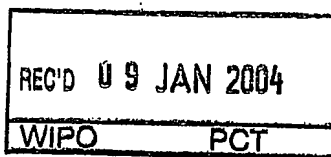




Rec'd 261/270 06 JUN 2005 #2



INVESTOR IN PEOPLE



The Patent Office
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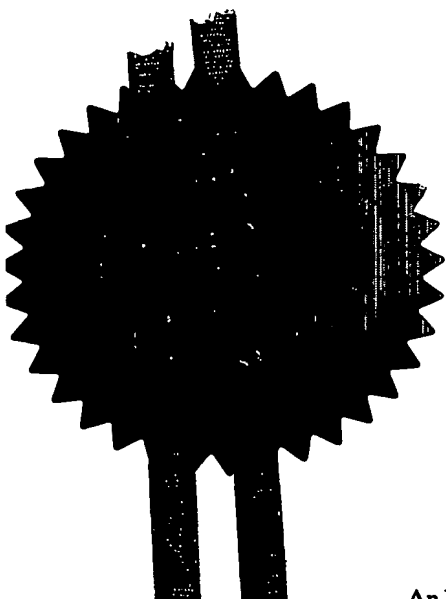
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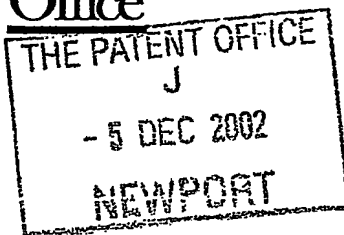
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Dated 23 December 2003



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Request for grant of a patent

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The Patent Office

Cardiff Road
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NP9 1RH

1. Your reference	AJC/P101253GB		
2. Patent application number (The Patent Office will fill in this part)	0228322.4		
3. Full name, address and postcode of the or of each applicant (underline all surnames)	British Nuclear Fuels Plc Risley WARRINGTON WA3 6AS		
Patents ADP number (if you know it)			
If the applicant is a corporate body, give the country/state of its incorporation	UK	350 108 001	
4. Title of the invention	SEPARATION OF METALS		
5. Name of your agent (if you have one)	Harrison Goddard Foote		
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	Belgrave Hall Belgrave Street LEEDS LS2 8DD		
Patents ADP number (if you know it)	14571001	7631310002	
6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)	Date of filing (day / month / year)
7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application		Date of filing (day / month / year)
8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (d))	Yes		

SEPARATION OF METALS

Field of the Invention

This invention relates to a method for the separation of metals from mixtures of metal oxides and relies on the selective reduction of certain oxides to the metals, whilst the other metals remain in the form of the oxides. The method of the present invention finds particular application in the separation of transition metals, lanthanides and actinides.

10 Background to the Invention

The prior art teaches the use of molten salts in the separation of metals and metal oxides in molten salt media. As used herein, the term "molten salts" is intended to cover salts such as lithium chloride which melts at an elevated temperature and also ionic liquids which typically are liquid at room temperature or which melt at a temperature up to about 300°C. Such techniques have found particular application in the nuclear industry, where two well-established processes are available for the treatment of irradiated nuclear fuel.

The first of these processes, the Dimitrovgrad SSC-RIAR process, makes use of chemical oxidants (chlorine and oxygen gases) to react with powdered uranium dioxide fuel to form higher oxidation state compounds such as UO_2Cl_2 which are soluble in the molten salt. In an electrochemical cell the uranium compounds are reduced to UO_2 at the cathode, forming a solid deposit. This process has both technical and environmental limitations.

The second process, developed by the Argonne National Laboratory (ANL) is fundamentally an electrefining technology which uses current flow to anodically oxidise uranium to form uranium ions in the molten salt electrolyte. At the cathode the uranium is reduced and electrodeposited as uranium metal.

The ANL process requires a metal feed. If oxide fuels are to be treated, it is necessary to reduce the uranium oxide (usually UO_2 pellets) to the metal. This reduction process is carried out chemically, using lithium metal in a LiCl or LiCl/KCl molten salt at 500 to 600°C. Alternatively, a salt transport process can be used involving a Cu-Mg-Ca alloy and molten CaCl_2 salt. However, in both reduction methods the by-products, Li_2O and CaO respectively, need to be recovered from the molten salt phase by an electrolysis step. Effectively this means a two stage process.

A disadvantage of the lithium reduction process for producing a metallic feed from an oxide is the production of Li_2O by-product. This requires recycle to make the process economic, and this is done by an electrolytic recovery of lithium metal. Hence this is a two stage process, comprising a reduction step followed by a lithium recovery stage.

More recently, in EP-A-1088113, there is proposed a method for the removal of oxygen from a metal oxide wherein an electrode comprising the metal oxide is contacted with a molten salt, and a potential is applied which is lower than the deposition potential of the cation of the molten salt, thereby facilitating removal of oxygen from the metal oxide.

Subsequently, in the PCT patent application published under No WO-A-01/41152, there is disclosed a single step process for reducing to metallic form a metal oxide present in spent nuclear fuel, the process comprising cathodically electrolysing the oxide in the presence of a molten salt electrolyte, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of the metal from the cations present in the molten salt.

The process thereby involves the use of a single electrochemical process to reduce the metal oxide fuel to a metallic form, with oxygen, carbon monoxide and carbon dioxide produced as the only by-products. The potential of the cathode is maintained and controlled so that only oxygen ionisation occurs and not the deposition of the

cations (eg Ca ions) in the fused salt. Typically, the oxide comprises an actinide oxide, such as uranium oxide or irradiated uranium oxide.

This process was then developed and applied to the separation of metals from a mixture of metal oxides such as occurs in spent nuclear fuel, which is a frequent requirement in the nuclear power industry. Thus mixtures of uranium and plutonium oxides, together with the oxides of other actinide metals, may additionally be contaminated with oxides of other, chemically active, metals such as, for example, those associated with fission products. Co-pending patent application No PCT/GB02/02402 teaches a method for the treatment of irradiated fuel which allows for the separation of uranium, and metals more noble than uranium, from such mixtures as are found in spent nuclear fuel, and facilitates the provision of these metals in a form suitable for use as the feed in a molten salt electrorefining process, whilst ensuring that other, more electropositive, metals remain in the form of oxides.

The present inventors, however, recognised that there is frequently the requirement, both within the nuclear industry and the wider chemical industry, for the separation of metals from mixtures of metal oxides, and that the established technologies within these industries often provide inadequate means for the performance of such separations. Thus, whilst the prior art, as previously discussed, has focused largely on applications within the nuclear power industry and, most particularly, on processes involving actinide metals, it is often necessary, in a wide range of industries, to separate a large variety of metals, many of which are not members of the actinide series.

The present invention, therefore seeks to provide a method for the electrochemical separation of metals, the method relying on the different reduction potentials of different oxides which results in the reduction of one oxide to the free metal, whilst the other metal remains as the oxide. Examples of metals which might be separated in this way include transition metals, lanthanides and actinides.

Statements of Invention

Thus, according to the present invention, there is provided a process for the separation of metals, said metals being comprised as the metal oxides in a mixed oxide sample, the process comprising:

- 5 (i) adding the mixed oxide to a molten salt electrolyte and cathodically electrolysing the oxide, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of metal from the cations present in the molten salt, and the applied potential difference being such as to facilitate selective reduction of one metal oxide at the expense of other metal oxides; and
- 10 (ii) separating the metal from the remaining metal oxides.

The potential of the cathode is maintained and controlled so that only oxygen ionisation occurs and not the deposition of the cations (eg Ca ions) in the fused salt, and also to ensure that, whilst reduction of one of the metals occurs smoothly, the
15 other metals are not reduced and remain in the anode as oxides. The only by-products which are produced are oxygen, carbon monoxide and carbon dioxide gases.

The process may be applied to the separation of a wide variety of metals. Specific examples of metals which may be successfully separated in this way include metals
20 of the transition, lanthanide and actinide series which are comprised as the oxides in mixed oxide samples. The broad usefulness and versatility of the method is illustrated by its applicability to the separation of metals from mixtures of two or more metal oxides.

25 A specific example of a preferred application of the process is in the separation of hafnium, present as the oxide, in samples of zirconium oxide. Zirconium metal is widely used in the nuclear power industry in zircalloy cladding. However, hafnium serves as a poison in nuclear reactors and it is vital, therefore, that it should be removed from the zirconium metal prior to the incorporation of this material in
30 cladding. Its removal is facilitated by the process of the present invention, wherein a

suitable potential difference is applied in order to facilitate the reduction of zirconium oxide to zirconium metal whilst leaving the hafnium oxide unchanged.

5 The mixed oxide may be in any physical form, and this is generally dependent on the particular application from which it has resulted. For example, it may be provided as solid pieces of irregular size and shape, but it may also comprise a powder, an amorphous mass, or a dense solid agglomerate. In any event, the material may be treated according to the method of the present invention by connection to an electrical circuit such that it serves as the cathode during electrolysis. Connection to
10 the circuit may be effected by any of the standard means well known to those skilled in the art.

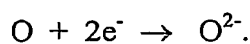
Preferably the mixed oxide is in contact with the cathode of an electrochemical cell. The cathode could be in the form of a mesh basket. The molten salt electrolyte may
15 be any suitable molten salt or mixture of such salts, for instance chloride salts, preferably CaCl_2 and/or BaCl_2 . The anode may be any suitable inert anode, such as carbon.

The separation step, whereby the metal is separated from the remaining metal oxides,
20 may comprise any of a number of techniques well known to those skilled in the art. Thus, for example, simple dissolution and solvent extraction techniques may be applicable; alternatively, heating and slagging methods could be appropriate. As a further alternative, additional electrochemical means may be employed to effect the separation.

25 Optionally, reduction of the selected metal oxide may be carried out in one particular molten salt, whilst separation of that metal from the other metal oxide or oxides is effected in a different molten salt composition. Alternatively, the two processes may be performed in the same molten salt.

Detailed description of the Invention

In order to carry out an embodiment of the present invention, an electrolytic cell is assembled which has a carbon anode and a mesh basket cathode. A mixed oxide sample is placed in the mesh basket. The electrolyte consists of a molten salt or a mixture of such salts comprising, for example, chloride salts such as CaCl_2 or BaCl_2 . A voltage is applied between the cathode and the anode. At the cathode the reaction involves the diffusion of oxygen atoms to the surface of the solid, followed by ionisation according to the reaction:



- 10 The oxide ions which are produced dissolve in the electrolyte and are transferred to the anode where they are re-oxidised to produce oxygen gas. Further by-products include carbon monoxide and carbon dioxide. The potential at the cathode may be controlled, via a third reference electrode, to ensure that the reaction occurring at the cathode is oxygen ionisation and not deposition of the cations in the fused salt, and
- 15 that only a selected metal oxide is reduced. Electrolysis at elevated temperatures results in an increased rate of oxygen diffusion, thereby also encouraging ionisation rather than metal deposition.

- After electrolysis the mixed oxide sample is left in the form of a metal/metal oxide solid mixture at the cathode, with one of the metals having been reduced to the metallic form, whilst the other metals remain in the form of their oxides. This metallic/metal oxide product is then subjected to a suitable separation treatment.
- 20

25

CLAIMS

1. A process for the separation of metals, said metals being comprised as the metal oxides in a mixed oxide sample, the process comprising:
 - 5 (i) adding the mixed oxide to a molten salt electrolyte and cathodically electrolysing the oxide, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of metal from the cations present in the molten salt, and the applied potential difference being such as to
10 facilitate selective reduction of one metal oxide at the expense of other metal oxides; and
 - (ii) separating the metal from the remaining metal oxides.
2. A process as claimed in claim 1 wherein said mixed oxide sample comprises
15 a mixture of two or more metal oxides.
3. A process as claimed in claim 1 or 2 wherein metal oxides comprise oxides of metals from at least one of the transition metal, lanthanide or actinide series.
- 20 4. A process as claimed in claim 3 wherein said metals comprise zirconium and hafnium and said mixed oxide sample comprises mixed zirconium and hafnium oxides.
5. A process as claimed in any one of claims 1 to 4 wherein the mixed oxide is
25 provided as solid pieces of irregular size and shape, a powder, an amorphous mass, or a dense solid agglomerate.
6. A process as claimed in any preceding claim wherein the oxide is located in a mesh basket which forms the cathode.

30

7. A process as claimed in any preceding claim wherein the molten salt electrolyte comprises at least one chloride salt.

8. A process as claimed in claim 7 wherein the chloride salt is CaCl_2 or BaCl_2 .

5

9. A process as claimed in any preceding claim wherein the anode is a carbon anode.

10

10. A process as claimed in any preceding claim wherein the step of separating the metal from the remaining metal oxides is carried out by the use of dissolution and solvent extraction techniques, heating and slagging methods or electrochemical means.

15

11. A process as claimed in any preceding claim wherein said reduction of the selected metal oxide is carried out in one molten salt whilst separation of the metal from the other metal oxide or oxides is effected in a different molten salt composition.

20

12. A process as claimed in any one of claims 1 to 10 wherein said reduction of the selected metal oxide and said separation of the metal from the other metal oxide or oxides is performed in the same molten salt.

25

13. A process substantially as hereinbefore described and with reference to the accompanying description.

30

ABSTRACT

The invention provides a process for the separation of metals, the metals being comprised as the metal oxides in a mixed oxide sample, the process comprising: (i) adding the mixed oxide to a molten salt electrolyte and cathodically electrolysing the oxide, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of metal from the cations present in the molten salt, and the applied potential difference being such as to facilitate selective reduction of one metal oxide at the expense of other metal oxides; and (ii) separating the metal from the remaining metal oxides. The process is applicable to mixed oxide samples comprising mixtures of two or more metal oxides, and is particularly useful for the separation of metals of the transition, lanthanide and/or actinide series comprised in mixed oxide samples. A particular application is in the separation of zirconium and hafnium comprised in mixed zirconium and hafnium oxides, the removal of hafnium facilitating the use of the zirconium in fuel cladding for use in the nuclear power industry.

P101253GB.3